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(21) International Application Number: PCT/SE97/01087 (22) International Filing Date: 18 June 1997 (18.06.97) (30) Priority Data: 9602466-6 20 June 1996 (20.06.96) SE (71) Applicant (for all designated States except US): McWHORTER TECHNOLOGIES AB [SE/SE]; P.O. Box 55, S-431 21 Mölndal (SE). (72) Inventors; and (75) Inventors/Applicants (for US only): JOHANSSON, Mikael [SE/SE]; Pomonagatan 4, S-431 42 Mölndal (SE). BAKKELUNN, Terje [NO/SE]; Brattåsvägen 89, S-438 32 Landvetter (SE). JÖNSSON, Erik, Sonny [SE/SE]; Tomtebgatan 1, Uppg. 2 III, S-113 39 Stockholm (SE). (74) Agents: GRAUDUMS, Valdis et al.; Albihn West AB, P.O. Box 142, S-401 22 Göteborg (SE).		(81) Designated States: CA, CZ, HU, JP, NO, PL, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>In English translation (filed in Swedish).</i>
(54) Title: PHOTOPOLYMERIZABLE POLYESTER COMPOSITION AND PROCESS FOR THE PRODUCTION THEREOF		
(57) Abstract The invention pertains to a curable polyester composition comprising an ethylenically unsaturated polyester and a co-monomer. The composition is primarily distinguished by the polyester and/or the co-monomer being terminated with at least one bulky, and/or hydrogen donating, monofunctional alcohol. The invention is also directed to a lacquer or a paint formulation comprising a polyester based binder composition in accordance with the invention.		

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PHOTOPOLYMERIZABLE POLYESTER COMPOSITION AND PROCESS FOR
5 THE PRODUCTION THEREOF

TECHNICAL FIELD:

10 The invention pertains to a photopolymerizable polyester composition comprising an ethylenically unsaturated polyester and a comonomer. The invention further relates to a lacquer or paint comprising the polyester composition and a method for its production.

15 BACKGROUND OF THE INVENTION:

When lacquering surfaces of materials, for instance in the furniture industry, the use of paint and lacquer comprising polymer compositions which may be cured by radiating the
20 surface with ultraviolet light, so called UV-light, presents major advantages. Such polymer compositions thereby act as a binder and permit the paint or lacquer to be coated, sprayed, or applied in some other manner to the surface of the material. Subsequent radiation treatment of
25 the surface with UV-light produces a hard coating with good flexibility, wear strength, and good resistance to chemicals. By UV-light is thereby meant light in a wave length range of 200-500 nm. The UV-light which is commonly used for curing paints and lacquers is usually within the
30 wave length range of 200-400 nm.

Curing by ultraviolet light implies very rapid curing processes and further makes it possible to use paint- and lacquer compositions which are free from organic solvents.
35 Accordingly, considerable advantages are achieved with regard to the working environment, since handling of solvents is avoided. Additionally, emissions of environmentally harmful components to the surroundings may be minimised by keeping the concentration of organic

compounds low. Further, the amount of lacquer or paint which is required in order to achieve a coating with good strength may often be reduced, as compared to lacquer and paint based on thermally curing binder compositions.

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The quality of the treated surface is to a high degree dependent on the molecular weight of the binder, such that binders with a high molecular weight and thereby also a high viscosity, produce high quality surfaces. For this reason, thermosetting binder compositions are usually diluted with organic solvents in order to make it possible to apply them to a surface. With a high quality of a treated material surface is meant that the surface meets the requirements for the above mentioned quality properties, namely hardness, flexibility, wear strength, adhesion and chemical resistance.

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Previously known, commonly available binder compositions for use in photo polymerisation are based on different acrylic oligomers and/or -monomers. Paint- and lacquer systems containing such binder compositions have high reactivity and produce treated material surfaces with good quality properties. The freedom to choose the method of application is, however, heavily restricted by considerations which have to be made regarding environmental and health hazards in connection with such systems. In addition, such paints and lacquers require the use of special protective equipment in order to reduce the risks associated with the application.

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Since those acrylate based lacquers and paints which show the highest reactivity and provide the best quality for the treated material surface are particularly troublesome from an environmental and health point of view, there exists a great need of finding an alternative system which retains the good qualities but have less hazardous properties.

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A further, previously known binder composition consists of a system comprising a combination of unsaturated polyester and styrene where the styrene monomer reacts with the polyester in a curing process. Such a system exhibits good reactivity and the treated material surface which is obtained is of high quality. A problem is, however, that the styrene monomer is volatile. Accordingly, and as in the case with the acrylate based lacquers and paints, the major disadvantage with a styrene containing system is the risks and problems regarding health and environment connected therewith.

In order to avoid using styrene or acrylates, the polymerisation of unsaturated polyester with other reactive monomers has been proposed. Some examples of such polymerisation are, for instance, given in EP 0 322 808, US 5 340 653, US 5 334 456 and US 5 334 455. A great disadvantage and a limitation with these types of binders is, however, that they show comparatively low reactivity. In particular, the reactivity in air is insufficient. Furthermore, it is a problem with these known systems that a surface which has been treated with a paint or lacquer remains tacky even after curing at normal radiation doses if the treatment has been carried out in air. This is due to the fact that oxygen in the air inhibits the curing reaction.

In an article with the title "Some practical aspects of Maleate/Vinyl ether systems in wood coating application" published in RadCureLetter no. 3, 1996, binder systems based on maleate/vinyl ether-combinations are described. According to the article, such systems exhibit a lower reactivity than acrylate based binder systems. This is said to be due to the low reactivity of the maleate/vinyl systems, since the maleic acid derivative and the vinyl ether form a charge-transfer-complex before the

polymerisation takes place. In this manner, the reactivity of the system is strongly dependent on the relation between the concentrations maleate:vinyl ether. It is said that the reactivity may be increased by increasing the radiation dose when curing the system. The terminal group of the polyester is only said to have an effect on parameters such as viscosity and Tg. There is no suggestion whatsoever that the choice of the terminal group affects the reactivity of the system.

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Accordingly, there exists a need for a reactive photopolymerisable binder system for paints and lacquers, having good properties from an environmental, a health, and a quality point of view.

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SUMMARY OF THE INVENTION:

With the present invention a polyester composition of the initially mentioned kind has been achieved, which polyester composition is well suited for use as a binder in different paint and lacquer compositions. With the polyester composition in accordance with the invention, the problems associated with previously known binders for paint and lacquers have been considerably reduced.

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A photopolymerisable polyester composition synthesised in accordance with the invention is primarily characterised by the polyester and/or the co-monomer being terminated with at least one bulky and/or hydrogen donating mono-functional alcohol.

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DETAILED DESCRIPTION OF THE INVENTION:

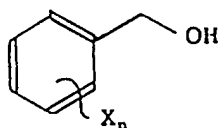
By terminating unsaturated polyester molecular chains with bulky and/or hydrogen donating, mono-functional alcohols, it has surprisingly been shown that the reactivity in a

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binder system containing such polyester molecular chains can be considerably increased. In this context, the term bulkiness is taken to mean that the alcohol exhibits structural elements having branched aliphatic and/or substituted aromatic groups, wherein the structural elements are bonded to the OH-group in the alcohol. The two terminal alcohol groups of the polyester molecular chain may be either identical, or different.

Some examples of useful aromatic terminal groups are:

benzyl alcohol, and groups having the general structural formula



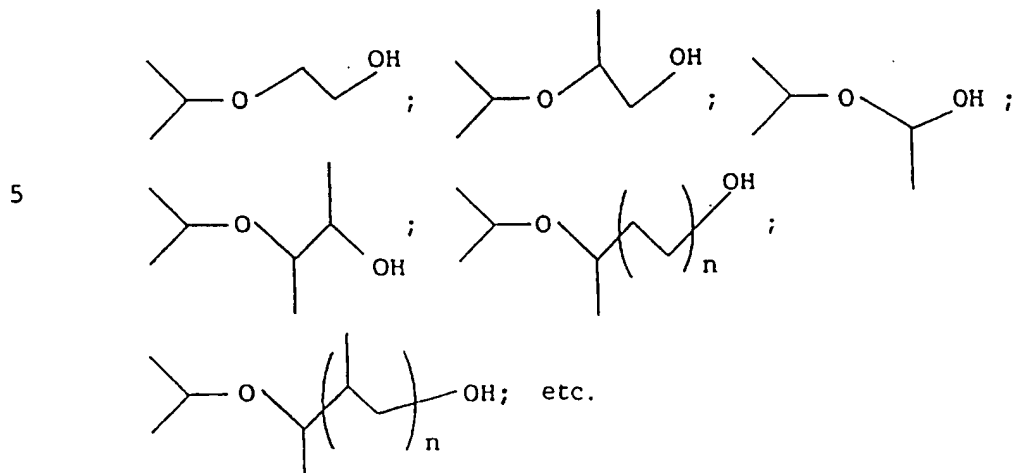
Where X may be alkyl, aryl, alkoxy, aryloxy, and corresponding thio-groups. X is preferably an electron donor.

Further, aliphatic terminal alcohols may be used having the general formula:

$R_3 - O - R_4 - OH$ where

R_4 and R_3 are substituents which define the number of $(CH_2)_n$ -groups, and the degree and type of branching of the structure. The number $n = 1-12$, preferably 1-3.

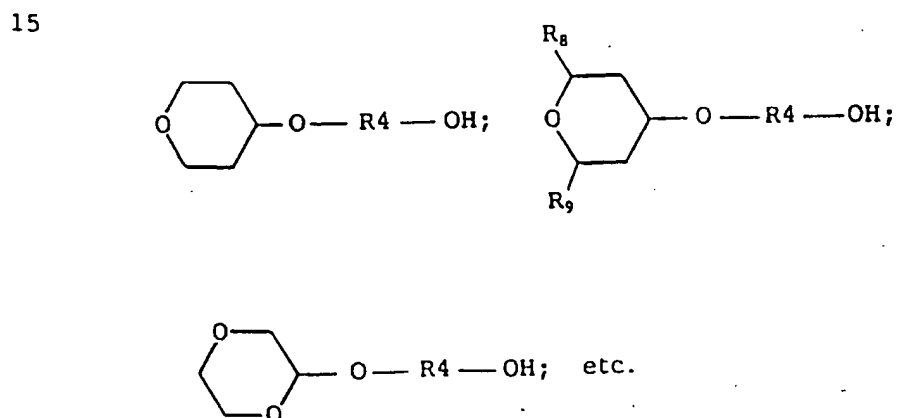
Some examples of suitable aliphatic branched alcohols are:



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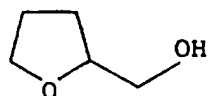
In addition the R₄ - substituent may be methyl, ethyl, n-propyl, butyl, etc.

Some other useful aliphatic alcohols are heterocyclic or cyclo-aliphatic alcohols such as:



where $R_4 = (CH_2)_n$, and $n = 1-12$, preferably 1-3; R_8 , R_9 = alkyl substituents, preferably methyl, ethyl, propyl or butyl.

5 Cyclic alcohols having 5-, 4-, and 7- atom rings may also be used. An example of an alcohol with a 5-atom ring is:

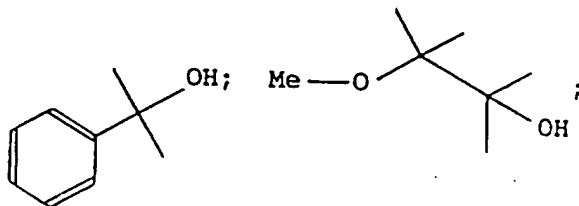
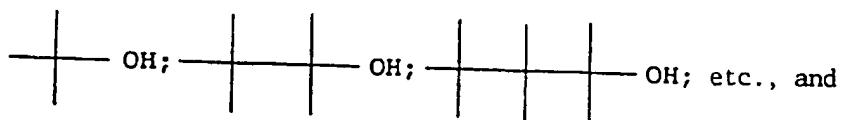


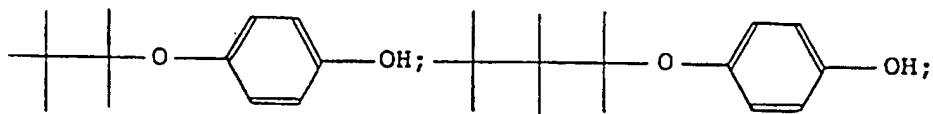
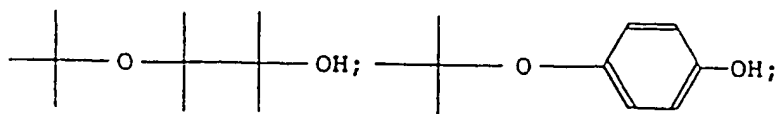
(tetrahydrofurfuryl alcohol)

10 Additionally, alkyl substituted tetrahydrofurfuryl alcohols, and the corresponding may also be used.

15 The term hydrogen donor refers to structural elements bonded to the OH-group and having abstractable hydrogen atoms. Hydrogen atoms showing particularly high reactivity are so called α -hydrogen atoms in electronegative hetero atoms such as -O-, -S-, -N-, -P-, amides, carbamates, or corresponding active functional organic groups.

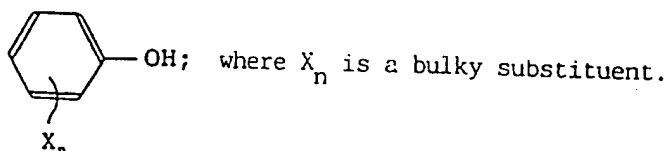
20 All the above mentioned bulky alcohols are hydrogen donors. However, bulky alcohols having all abstractable hydrogen atoms blocked may be useful. Some examples of bulky alcohols which are not hydrogen donors are:





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etc., and $\text{R}_{11} \text{---} \text{O} \text{---} \text{C}_6\text{H}_4 \text{---} \text{OH}$; where R_{11} is a bulky substituent and

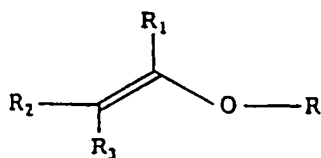


10 Other similar compounds may also be used.

The advantageous effect of bulky, hydrogen donating, monofunctional alcohols is apparent both in systems with unsaturated polyester and mono- and multi-functional alkenyl ethers, as well as in systems with unsaturated polyester and mono- and multi-functional alkenyl esters.

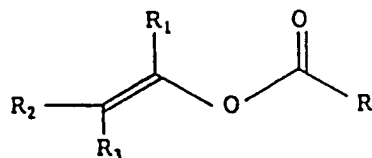
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An alkenyl ether is taken to be a compound having the general structure:



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An alkenyl ester has the general structure:



5 where R₁, R₂, and R₃ = H, or a C₁ - C₁₈ alkyl-group and R is the backbone of the ether or ester.

10 Further, it has been shown that binder systems with unsaturated polyester and systems with n-alkenylamines or n-alkenylamides also show increased reactivity as compared to conventional binders based on unsaturated polyester.

The co-monomer or -oligomer which is used may either be mixed with the unsaturated polyester, or be chemically incorporated therein.

15 It has also been shown to be possible to further increase the reactivity for a binder system in accordance with the invention by performing the synthesis of the unsaturated polyester under conditions that will simultaneously produce fractions of oligomeric type, comprising the previously mentioned terminal alcohol.

20 An additional advantage with a polyester composition in accordance with the invention is that it exhibits very good reactivity in air. A binder system consisting of the polyester composition in accordance with the invention is hence so reactive that the problem with oxygen inhibition and tacky, incompletely hardened material surfaces has been
25 substantially removed.

Binder compositions comprising unsaturated polyesters may be used both in systems without a solvent and in water emulsion systems. Accordingly, emulgated unsaturated polyesters may be produced and may be successfully used in combination with alkenyl ethers, alkenyl esters, n-alkenyl amines, or n-alkenyl amides for spray coating of three-dimensionally shaped articles.

There are several different reasons why the use of a binder system emulgated in water is advantageous. For one thing, it means that the molecular weight of the binder and hence its viscosity is reduced to being of minor importance. It also implies that even binders having a high molecular weight and viscosity may be used and may, with good results, be applied using conventional methods such as, for instance, spraying. The reason why it is desirable to use binders with a high molecular weight is that such binders generally produce a coated material surface having superior end properties when compared to binders having a low molecular weight.

When treating three-dimensional surfaces, spraying is the application method providing the best results. Since good surface qualities are evidently sought after even for three-dimensionally shaped objects, it is naturally a major advantage to be able to spray paints and lacquers comprising binders having a high molecular weight.

By means of the invention, it is thus possible to obtain a binder system based on an unsaturated polyester and a co-monomer, wherein the system exhibits an increased reactivity when compared to previously known systems based on unsaturated polyester. The increased reactivity will appear both if the co-monomer is in the form of a separate component in the system and if it is chemically incorporated into the polyester.

5 The reactivity achieved for a system in accordance with the invention is on the same level as the reactivity obtained in the earlier known acrylate systems. In addition, the environmental and health problems associated with the use of acrylates are reduced to a considerable degree with the system in accordance with the invention.

10 Commonly used curing equipment, for instance in the furniture industry, is dimensioned for UV-doses between 300-500 mJ/cm². Since the radiation intensity of the UV-lamps which are being used diminishes after a while, this will in practice mean that a finished lacquer or paint containing a binder in accordance with the invention should be curable at radiation doses below 300 mJ/cm². In this context, a lacquer or paint is regarded to exhibit
15 sufficient reactivity if the lacquer surface which is obtained fulfils predetermined demands on qualities such as hardness, flexibility, wear strength, adhesion and chemical resistance. In practice, however, it is impossible to reach a rate of conversion or a curing degree with regard to
20 unsaturated sites in the finished lacquer or paint which is 100%. The necessary degree to which the curing reaction has to be carried out in order to achieve satisfactory properties in a coated material surface depends on the composition of the binder system which is used. Naturally,
25 the demands which are put on the coated material surface vary depending on the intended use for the surface.

30 A binder composition in accordance with the invention is initially a liquid and is cured after having been applied to a material surface, the curing being effected by radiation with ultra violet light. The application of a lacquer, or a paint containing the binder composition to a material surface may thereby be carried out using any suitable known technique. Some examples of such known

techniques are spraying, roller coating , curtain coating or doctor blade coating.

5 The unsaturated polyester in the binder composition is crosslinked in the curing process by having its unsaturated sites react with unsaturated sites in the co-monomer comprised in the binder composition. In order to accomplish curing, it is necessary that the binder composition in addition to the polyester and the co-monomer, also contains a photo-initiator. Some suitable photo-initiators are, for example, isobutyl benzoine ether, mixtures of butyl isomers of butyl benzoine ether, alfa, alfa-diethoxy acetophenone and alfa, alfa-dimethoxy-alfa-phenyl acetophenone. Some further examples of useful photo-initiators are to be found in US A-4,017,652.

15 The ethylenically unsaturated polyester may be an unsaturated polyester polymer, an unsaturated polyester oligomer or a mixture of those. The production of unsaturated polyesters is a well known technique and will not be described here.

20 Useful unsaturated polyester are usually esters of ethylenically unsaturated carboxylic acids and organic polyalcohols, also called organic polyols. Usually the starting materials are a carboxylic acid having an acid functionality of at least two, i.e. a di-carboxylic acid or its anhydride. Some examples of such unsaturated di-carboxylic acids and anhydrides are maleic acid, maleic acid anhydride, fumaric acid and itaconic acid.

30 Further, in a binder composition in accordance with the invention it is possible to use unsaturated polyesters wherein a saturated poly-carboxylic acid constitutes one part of the carboxylic acid component. Some examples of saturated poly-carboxylic acid which may be used are

phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, tetrahydrophthalic acid, hexahydrophthalic acid, tetrachlorophthalic acid, adipic acid, azelaic acid, sebacic acid, succinic acid, glutaric acid, malonic acid, pimelic acid, suberic acid, 2,2-dimethylsuccinic acid, 3,3-dimethylglutaric acid and 2,2-dimethylglutaric acid. Where appropriate, anhydrides of the mentioned poly-carboxylic acids may of course also be used.

Mono-functional carboxylic acids, such as benzoic acid and paratertiary butyl benzoic acid, etc., may be used.

Some examples of organic polyols which are suitable for the production of an unsaturated polyester comprise ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, glycerol, trimethylolpropane, pentaerythritol, sorbitol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, 1,2-bis(hydroxyethyl)cyclohexane and 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate. Preferred organic polyols are the diols. A particularly preferred polyol is diethylene glycol, since it is readily available and comparatively inexpensive. Organic polyols having a hydroxylic functionality greater than 2 can be used in the preparation of the unsaturated polyester. Preferably, however, the major part, if not all of the unsaturated polyester, consists of linear polyester molecules. For this reason, the use of diols is preferred.

The molecular weight of the unsaturated polyesters which are used in the binder composition in accordance with the invention may vary within a wide range. Accordingly, the molecular weight may be anything from 300 g/mol all the way up to 50,000 g/mol.

When the co-monomer in the binder composition consists of a alkenyl ether, alkenyl ether monomers having 1-4 alkenyl ether groups per molecule of the alkenyl ether component are used. It has surprisingly been shown that terminal
5 alcohols in accordance with the invention make it possible to obtain good mechanical properties and, in addition, a high reactivity even at a mean functionality of the alkenyl ether components being considerably lower than 2. As has
10 been previously mentioned, the alkenyl ether component may exist in the form of a separate component which is mixed with the unsaturated polyester. Alternatively, the alkenyl ether may be chemically incorporated in the unsaturated polyester.

In the polyester composition, the relative amounts of the
15 unsaturated polyester and the alkenyl ether are such that the relation between the number of carbon-carbon-double bonds, i.e. the number of unsaturations in the unsaturated polyester and the number of carbon-carbon-double bonds, i.e. the number of unsaturations in the alkenyl ether is
20 between 0.7-1.3, and preferably between 0.9-1.1.

Those alkenyl ethers which may be utilised separately in a mixture with unsaturated polyester are, for instance, ethylvinyl ether, propylvinyl ether, n-butylvinyl ether, iso-butylvinyl ether, tert-butylvinyl ether,
25 hydroxybutylvinyl ether, tert-amylvinyl ether, 1,4-cyclohexane-dimethanol-divinylether, n-dodecylvinylether, cyclohexane-dimethanol-monovinyl ether, cyclohexylvinyl ether, ethyleneglycol-monovinyl ether, diethyleneglycol-divinyl ether, butanediol-divinyl ether, 2-ethylhexyl-vinyl ether, dipropyleneglycol-divinyl ether, tripropyleneglycol-divinyl ether,
30 1,6-hexanediol-divinyl ether, n-octadecylvinyl ether, ethyleneglycol-butylvinyl ether, triethyleneglycol-divinyl ether, triethyleneglycol-methylvinyl ether, ethyleneglycol-divinyl ether,

diethyleneglycol-monovinyl ether, hexanediol-monovinyl ether, and tetraethyleneglycol-divinyl ether.

5 Other suitable alkenyl ethers are propenyl ethers, whereby all existing mono-, di-, and tri-propenyl ethers having the above mentioned basic structures may be used, as well as, where appropriate, cis-, trans-, and iso- forms.

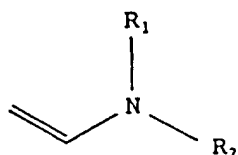
10 Alkenyl ethers existing as chemically incorporated groups which are bonded to the molecular chain of the unsaturated polyester may be obtained from the previously recited saturated carboxylic acids and unsaturated carboxylic acid anhydrides, and the earlier mentioned organic polyols. One way of linking the alkenyl ether to the unsaturated polyester is by using an organic diisocyanate.

15 It is further possible to achieve good results using an amine as starting material which is subsequently derivatised in order to obtain the corresponding n-alkenyl-amine. Some suitable amines are, for instance, toluene-2,4-amine, toluene-2,6-amine and mixtures thereof; or diphenylmethane-4,4'-aminediphenyl-methane-2,4'-amine and mixtures thereof; or paraphenylene-amine, biphenyl-amine, 3,3'-dimethyl-4,4'-diphenylene-amine, tetramethylene-1,4-amine, hexamethylene-1,6-amine, 2,2,4-trimethylhexane-1,6-amine, lysin-methyl-ester-amine, bis(amino-ethyl)fumarate, isophorone-amine, ethylene-amine, dodecane-1,12-amine, 20 cyclobutane-1,3-amine, cyclo-hexane-1,3-amine, cyclohexane-1,4-amine and mixtures thereof; methyl-cyclohexyl-amine hexahydro-toluene-2,4-amine, hexahydro-toluene-2,6-amine, and mixtures thereof; hexahydrophenylene-1,3-amine, hexahydrophenylene-1,4-amine, and mixtures thereof; 30 perhydrodiphenylmethane-2,4'-amine, perhydrodiphenylmethane-4,4'-amine and mixtures thereof. The resulting unsaturated polyester comprises urethane groups.

Similarly, the starting material may be an amide which has been derivatised to an n-alkenyl amide. Suitable amides are those amides corresponding to the previously mentioned amines.

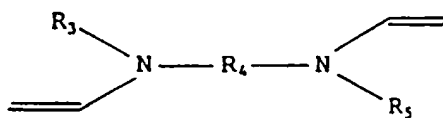
- 5 The intended n-alkenyl-amines may be mono-functional, di-functional, or multi-functional. Aliphatic compounds, as well as their cyclic forms, may be used. Mono-functional n-alkenyl-amines have the general structural formula:

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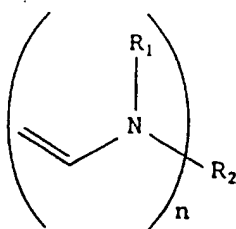
Where $R_1, R_2 = H, \text{ alkyl, or aryl.}$

- 15 Di-functional n-alkenyl-amines have the general structural formula:



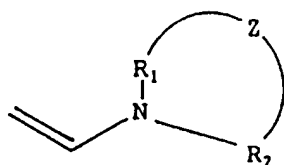
- 20 where $R_3, R_5 = H, \text{ alkyl, or aryl.}$

Multi-functional n-alkenyl-amines have the general structural formula:



- 5 wherein $R_1, R_2 = H$, alkyl, or aryl and $1 < n < 7$ - R_2 has a greater mean functionality with respect to amino groups in the pre-oligomeric chain than the corresponding mono-unctional n-alkenyl amine.

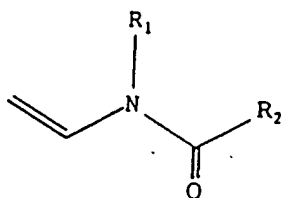
- 10 The cyclic n-alkenyl-amines have the general structural formula:



wherein $R_1, R_2 =$ alkyl, or aryl and Z defines the ring size and may comprise one or more hetero atoms.

- 15 The n-alkenyl-amides which may be utilised have structures corresponding to that of the n-alkenyl-amines. Accordingly, there exist mono-functional, di-functional and multi-functional n-alkenyl-amides, and their corresponding closed ring forms.

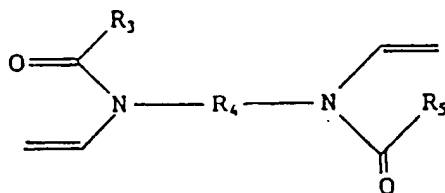
- 20 The mono-functional n-alkenyl-amides have the general structural formula:



wherein $R_1 = R_2 = H$, or wherein $R_1 = H$, $R_2 = \text{alkyl}$, or aryl.

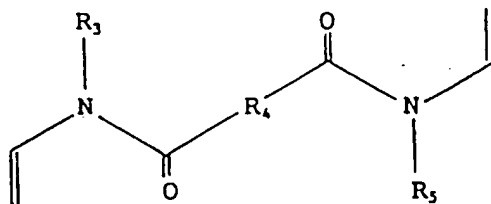
The di-functional n-alkenyl-amides have the general structural formula:

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or

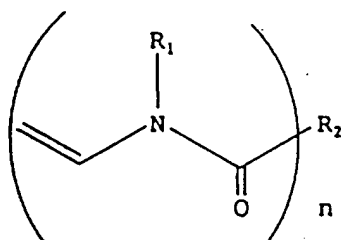
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wherein $R_3 = R_5 = H$, alkyl, or aryl.

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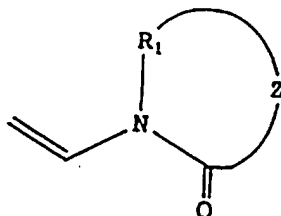
The multi-functional n-alkenyl-amides have the general structural formula:



20

wherein $R_1 = H$, alkyl, or aryl; $R_2 = \text{alkyl}$, or aryl and $1 < n < 7$.

The cyclic n-alkenyl-amides have the general structural formula:



wherein R₁ = alkyl, or aryl and Z defines the ring size and indicates the possible existence of hetero atoms.

Apart from the given examples of amines and amides, the corresponding cis-, trans-, and iso-forms of the propenyl-compounds may also be used.

Those alkenyl esters which are suitable as co-monomers are, for example, vinyl esters such as vinyl-formamate, vinyl-acetate, vinyl-propionate, vinyl-butyrate, vinyl-caproate, vinyl-caprylate, vinyl-caprate, vinyl-laurate, vinyl-myristate, vinyl-palmitate, vinyl-stearate, vinyl-chloroacetate, vinyl-adipate, vinyl-acrylate, vinyl-methacrylate, vinylchrotonate, vinyl-sorbate, vinyl-pivalate, vinyl-benzoate, vinyl-cinnamate, vinyl-p-tert-butylbenzoate.

In addition to the unsaturated polyester and the co-monomer, the binder composition may comprise other ethylenically unsaturated monomers or oligomers. Some examples are vinyl-monomers such as vinyl acetate, styrene, vinyl toluene, divinyl benzene, methylvinyl ether, ethylvinyl ether, and butyl-vinyl ether; acrylic and methacrylic esters such as methyl (meth)acrylate, ethyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, glycidyl (meth)acrylate, ethylene glycol di(meth)acrylate,

diethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, glycerol di(meth)acrylate, glycerol tri(meth)acrylate, 1,3-propylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,2,4-butanetriol tri(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,4-cyclohexanediol di(meth)acrylate, 1,4-benzenediol di(meth)acrylate, pentaerythritol tetra(meth)acrylate, 1,5-pentanediol di(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolpropane tri(meth)acrylate, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate, isobornyl (meth)acrylate, and tetrahydrofurfuryl (meth)acrylate; (meth)acrylates derived from aromatic glycidyl ethers such as bisphenol-A-diglycidyl ether and aliphatic glycidyl ethers such as butanediol diglycidyl ether, specific examples of which include 1,4-butanediol diglycidylether di(meth)acrylate, bisphenol-A-diglycidylether di(meth)acrylate and neopentylglycol diglycidylether di(meth)acrylate; and acrylic or methacrylic amides such as (meth)acrylamide, diacetone (meth)acrylamide, N(beta-hydroxyethyl) (meth)acrylamide, N,N-bis(beta-hydroxyethyl) (meth)acrylamide, methylene bis(meth)acrylamide, 1,6-hexamethylene bis(meth)acrylamide, diethylenetriamine tris(meth)acrylamide, bis(gamma-(meth)acrylamidepropoxy) ethane and beta-(meth)acrylamide ethylacrylate.

DESCRIPTION OF EXAMPLES:

The invention will in the following be described by means of a number of examples which are intended to more closely illustrate the invention.

In the examples:

Cardura E10 is a commercially available epoxy ester having the chemical formula 2,2-dimethyl glycidyl propionate;

5 Esacyre KIP 100F is a commercially available photo initiator sold by Fratelli & Lamberti S.p.A., Italy;

Rapicure DVE-3 is a commercially available triethylene glycol sold by International Specialty Products, USA;

DVAP is a commercially available divinylester adipate from Shinetsu Vinyl Acetate Co. Ltd, Japan;

10 Darocur 1173 is a commercially available photo initiator from Ciba-Geigy, Switzerland; and

Irganox B225 is a commercially available mixture of anti oxidant and phosphite from Ciba-Geigy.

Example 1

15 Description of preparing a simple, UV-curing oligomer. As terminal mono-functional alcohol, the following compounds have been used: 2-ethylhexanol in Example 1a), bensyl alcohol in Example 1b), n-butanol in Example 1c), and ethyleneglycol monopropyl ether in Example 1d).

20 1a) A reaction vessel equipped for distillation and with a supply of inert gas is charged with 159 g (1.5 mol) diethylene glycol, 294 g (3.0 mol) maleic acid anhydride, and 0,10 g hydroquinone.

The reaction mixture is heated to 130°C and is kept at that temperature for 15 minutes. After the lapse time, 390 g (3.0 mol) 2-ethylhexanol is added. The temperature is gradually raised to 230°C. When increasing the temperature, the head temperature of the distillation column must not exceed 100°C. When 54 ml water has been removed and the acid value is less than 10 mg KOH/gm, the oligomer which has been produced is cooled to 150°C and 28.0 g (0.11 mol) Cardura E10 is added. The synthesis is terminated when the acid value is less than 2 mg KOH/g.

1b) A reaction vessel equipped for distillation and with a supply of inert gas is charged with 159 g (1.5 mol) diethylene glycol, 294 g (3.0 mol) maleic acid anhydride, and 0.10 g hydroquinone.

The reaction mixture is heated to 130°C and is kept at that temperature for 15 minutes. After the lapse time, 324 g (3.0 mol) bensyl alcohol is added. The temperature is gradually raised to 230°C. When increasing the temperature, the head temperature of the distillation column must not exceed 100°C. When 54 ml water has been removed and the acid value is less than 10 mg KOH/gm, the oligomer which has been produced is cooled to 150°C and 28.0 g (0.11 mol) Cardura E10 is added. The synthesis is terminated when the acid value is less than 2 mg KOH/g.

1c) A reaction vessel equipped for distillation and with a supply of inert gas is charged with 177.0 g (1.5 mol) 1,6-hexanediol, 294 g (3.0 mol) maleic acid anhydride, and 0.10 g hydroquinone.

The reaction mixture is heated to 130°C and is kept at that temperature for 15 minutes. After the lapse time, 222 g (3.0 mol) n-butanol is added. The temperature is gradually raised to 230°C. When increasing the temperature, the head

temperature of the distillation column must not exceed 100°C. When 54 ml water has been removed and the acid value is less than 10 mg KOH/gm, the oligomer which has been produced is cooled to 150°C and 28.0 g (0.11 mol) Cardura E10 is added. The synthesis is terminated when the acid value is less than 2 mg KOH/g.

ld) A reaction vessel equipped for distillation and with a supply of inert gas is charged with 114.0 g (1.5 mol) propylene glycol, 294 g (3.0 mol) maleic acid anhydride, and 0.10 g hydroquinone.

The reaction mixture is heated to 130°C and is kept at that temperature for 15 minutes. After the lapse time, 312 g (3.0 mol) ethyleneglycol monopropyl ether is added. The temperature is gradually raised to 230°C. When increasing the temperature, the head temperature of the distillation column must not exceed 100°C. When 54 ml water has been removed and the acid value is less than 10 mg KOH/gm, the oligomer which has been produced is cooled to 150°C and 28.0 g (0.11 mol) Cardura E10 is added. The synthesis is terminated when the acid value is less than 2 mg KOH/g.

Example 2

Description of the production of unsaturated polyester intended for UV-curing. In Examples 2a) and 2b) bensyl alcohol was used as mono-functional terminal alcohol. In Example 2c) a different charging order was used.

2a) A reaction vessel equipped for distillation and with a supply of inert gas is charged with 429.4 g (4.05 mol) diethylene glycol, 487.5 g (4.2 mol) fumaric acid, 196.1 g (1.9 mol) neopenthyl glycol, 50.0 g (0.35 mol) adipic acid, 177.4 g (1.1 mol) isophthalic acid, and 0.15 g hydroquinone.

The reaction mixture is gradually heated to 175°C. During the temperature increase, the head temperature of the distillation column must not exceed 100°C. When the acid value is 90 mg KOH/g, the formed oligomer is cooled to 130°C and 139.5 g (1.1 mol) 2-ethylhexanol is added. The reaction mixture is heated gradually to 230°C. During the temperature increase, the head temperature of the distillation column must not exceed 100°C. When the acid value is less than 20 mg KOH/g, the formed oligomer is cooled to 150°C and 135.2 g (0.54 mol) Cardura E10 is added. The synthesis is terminated when the acid value is less than 2 mg KOH/g.

2b) A reaction vessel equipped for distillation and with a supply of inert gas is charged with 429.4 g (4.05 mol) diethylene glycol, 487.5 g (4.2 mol) fumaric acid, 196.1 g (1.9 mol) neopentyl glycol, 50.0 g (0.35 mol) adipic acid, 177.4 g (1.1 mol) isophthalic acid, and 0.15 g hydroquinone.

The reaction mixture is gradually heated to 175°C. During the temperature increase, the head temperature of the distillation column must not exceed 100°C. When the acid value is 90 mg KOH/g, the formed oligomer is cooled to 130°C and 115.9 g (1.1 mol) 2-benzyl alcohol is added. The reaction mixture is heated gradually to 230°C. During the temperature increase, the head temperature of the distillation column must not exceed 100°C. When the acid value is less than 20 mg KOH/g, the formed oligomer is cooled to 150°C and 135.2 g (0.54 mol) Cardura E10 is added. The synthesis is terminated when the acid value is less than 2 mg KOH/g.

2c) A reaction vessel equipped for distillation and with a supply of inert gas is charged with 429.4 g (4.05 mol) diethylene glycol and 177.4 g (1.1 mol) isophthalic acid.

5 The reaction mixture is gradually heated to 230°C. During the temperature increase, the head temperature of the distillation column must not exceed 100°C. When the acid value is less than 2 mg KOH/g, the formed oligomer is cooled to 130°C and 50.0 g (0.35 mol) adipic acid, 196.1 g (1.9 mol) neopentyl glycol, 487.5 g (4.2 mol) fumaric acid, and 0.15 g hydroquinone are added. The reaction mixture is gradually heated to 175°C. During the temperature increase, the head temperature of the distillation column must not exceed 100°C. At an acid value corresponding to 150 mg KOH/g, the formed oligomer is cooled to 130°C and 115.9 g (1.1 mol) 2-benzyl alcohol is added. The synthesis is gradually heated to 230°C. During the temperature raise, the head temperature of the distillation column must not exceed 100°C. When the acid value is less than 20 mg KOH/g, the formed oligomer is cooled to 150°C and 135.2 g (0.54 mol) Cardura E10 is added. The synthesis is terminated when the acid value is less than 2 mg KOH/g.

Example 3

25 Unsaturated polyester synthesised in accordance with Example 2b) is mixed with a PEG-based emulsifier.

3a) Unsaturated polyester is synthesised in accordance with Example 2b).

30 3b) A reaction vessel equipped for distillation and with a supply of inert gas is charged with 1242.3 g (0.83 mol) polyethylene glycol 1500 and 181.4 g (1.24 mol) adipic acid.

5 The reaction mixture is slowly heated to 215°C. When the acid value is 35 mg KOH/g, the formed oligomer is cooled to 140°C and 175.7 g (0.83 mol) trimethylol propane diallyl ether and 0.7 g Irganox B225 are added. The reaction mixture is heated to 190°C. When the acid value is less than 20 mg KOH/g, the formed oligomer is cooled to 150°C and 125 g (0.5 mol) Cardura E10 is added. The synthesis is terminated when the acid value is less than 2 mg KOH/g.

10 3c) A reaction vessel equipped for emulsification is charged with 90 g polyester in accordance with Example 3a) and 10 g emulsifier in accordance with Example 3b). When the mixture has been well mixed, 35 g water is slowly added during vigorous stirring. After 10 minutes, an additional 65 g water is added.

15

20

Example 4

Reactivity and curing of Example 1, Example 2, and Example 3.

5

Table 1. Mixture ratios by weight for the components in the lacquer formulations in accordance with Examples 4a) - 4h).

10

15

20

	4a	4b	4c	4d	4e	4f	4g	4h
Polyester 1a	72.9							
Polyester 1b		71.3						
Polyester 1c			67.8					
Polyester 1d				68.7				
Polyester 2a					77.1			
Polyester 2b						76.5		
Polyester 2c							76.5	
Mixture 3c								39.3
DVE-3	27.1	28.7	32.2	31.3	22.9	23.5	23.5	10.7
Water	-	-	-	-	-			50

25

30

By reactivity is meant the radiation dose required to achieve surface scratch resistance in a dry film having a thickness of 45 μm . Accordingly, the reactivity of the different lacquer formulations were:

- 5 4a) 700-800 mJ/cm^2
- 4b) 250-300 mJ/cm^2
- 4c) more than 1000 mJ/cm^2
- 4d) 250-300 mJ/cm^2
- 4e) 500-600 mJ/cm^2
- 10 4f) 100 mJ/cm^2
- 4g) 200 mJ/cm^2
- 4h) 130-160 mJ/cm^2

15 The curing was performed using what is known as "a medium pressure mercury arc". A radiation source of this kind produces a typical mercury emission spectre. The light intensity was measured with a UVIMAP from EIT instruments. At a band speed of 10 m/min, the light intensity, measured in the area 320-400 nm, is 80-100 mW/cm^2 .

20 4% photo initiator Darocur 1173, and 100 ppm inhibitor parabenzoequinone were added to the mixtures in accordance with Examples 4a) - 4g). Both were calculated on dry weight.

25 4% photo initiator Esacure KIP 100F and 100 ppm inhibitor parabenzoequinone were added to the mixture in accordance with Example 4h). Both were calculated on dry weight. Before the UV-curing, the water was evaporated for 10 minutes at 50°C.

The molar ratio between the unsaturation in the vinyl ether (the co-monomer) and the ethylenical unsaturation in the polyester is 1:1.

5 Examples 4a), 4b), 4c), and 4d) show curing results for simple oligomers. The backbone is identical in 4a) and 4b), whereas a glycol is substituted in 4c) and 4d). This difference has, however, minimal influence on the curing results. The differences in curing result can be attributed to the choice of monofunctional terminal alcohol. Benzyl
10 alcohol (4b)) and ethylene glycol monopropyl ether (4d)) show the best results. These findings are in accordance with the present invention and show how bulky and/or hydrogen donating monofunctional terminal alcohols affect the reactivity in a positive direction.

15 In Examples 4e) and 4f) there is shown the curing results for unsaturated polyesters which have been terminated with 2-ethylhexanol and benzyl alcohol, respectively. The superior curing result for the benzyl alcohol is explained by the bulkiness and hydrogen donating ability of the
20 benzyl alcohol.

Examples 4f) and 4g) show the importance of the charging order. When compared to the mixture used in Example 4g), more oligomer containing benzyl alcohol, such as benzyl
25 alcohol-isophthalic acid-benzyl alcohol, is formed in Example 4f). Hence, it is evident that an oligomer of a bulky and/or hydrogen donating mono-functional alcohol may affect the curing reaction in a positive way.

From Example 4h) it can be learned that the curing result for a water emulsion of the mixture in accordance with
30 Example 4f) is satisfactory.

Example 5

Urethane modified unsaturated polyester intended for UV-curing. Example 5a) is carried out using 2-ethylhexanol and Example 5b) with benzyl alcohol as mono-functional terminal alcohol.

5a) A reaction vessel equipped for distillation and with a supply of inert gas is charged with 1126.0 g (10.6 mol) diethylene glycol, 1228.0 g (10.6 mol) fumaric acid, 1378.0 g (10.6 mol) 2-ethyl hexanol, and 0.35 g hydroquinone.

The reaction mixture is gradually heated to 230°C. During the temperature increase, the head temperature of the distillation column must not exceed 100°C. At an acid value of 6 mg KOH/g, the formed oligomer is cooled to 150°C whereafter 158.0 g (0.63 mol) Cardura E10 is added. The synthesis is terminated when the acid value is less than 2 mg KOH/g.

5b) A reaction vessel equipped for distillation and with a supply of inert gas is charged with 1126.0 g (10.6 mol) diethylene glycol, 1228.0 g (10.6 mol) fumaric acid, 1143.5 g (10.6 mol) benzyl alcohol, and 0.35 g hydroquinone.

The reaction mixture is gradually heated to 230°C. During the temperature increase, the head temperature of the distillation column must not exceed 100°C. At an acid value of 6 mg KOH/g, the formed oligomer is cooled to 150°C whereafter 158.0 g (0.63 mol) Cardura E10 is added. The synthesis is terminated when the acid value is less than 2 mg KOH/g.

Example 6

Unsaturated urethane modified polyester synthesised in accordance with Example 5b) mixed with a PEG-based emulsifier.

5 6a) Unsaturated urethane modified polyester synthesised in accordance with Example 5b).

6b) Polyethylene glycol based emulsifier in accordance with Example 3b).

10 6c) A reaction vessel equipped for emulsification is charged with 80 g polyester synthesised in accordance with Example 6a) and 20 g emulsifier in accordance with Example 6b). When the mixture has been well mixed, 35 g water is slowly added during vigorous stirring. After 10 minutes, an additional 65 g water is added.

15 Example 7

Reactivity and curing of Example 5 and Example 6.

Table 2. The mixing ratios in parts per weight for the components included in the lacquer formulations in accordance with Examples 7a) - 7c).

20

	7a	7b	7c
Polyester 5a	79		
Polyester 5b		79	
Mixture 6c			39.5
DVE-3	21	21	10.5
25 Water			50

By reactivity is meant the radiation dose required to achieve surface scratch resistance in a dry film having a thickness of 45 μm . Accordingly, the reactivity of the different lacquer formulations were:

- 5 7a) 500-600 mJ/cm^2
- 7b) 150-200 mJ/cm^2
- 7c) 200-250 mJ/cm^2

10 The curing was performed using what is known as "a medium pressure mercury arc". A radiation source of this kind produces a typical mercury emission spectre. The light intensity was measured with a UVIMAP from EIT instruments. At a band speed of 10 m/min, the light intensity, measured in the area 320-400 nm, is 80-100 mW/cm^2 .

15 4% photo initiator Darocur 1173, and 100 ppm inhibitor parabenzquinone were added to the mixtures in accordance with Examples 7a) and 7b). Both were calculated on dry weight.

20 4% photo initiator Esacure KIP 100F and 100 ppm inhibitor parabenzquinone were added to the mixture in accordance with Example 7c). Both were calculated on dry weight. Before the UV-curing, water was evaporated for 10 minutes at 50°C.

25 The molar ratio between the unsaturation in the vinyl ether (the co-monomer) and the ethylenical unsaturation in the polyester is 1:1.

Examples 7a) and 7b) show the curing results for a urethane modified polyester. The difference between 7a) which has been terminated with 2-ethylhexanol and 7b) which

has been terminated with benzyl alcohol is due to the bulkiness and hydrogen donating ability of the benzyl alcohol.

5 Example 7c) shows that a water emulsion of the mixture in accordance with 7b) exhibits satisfactory curing properties.

Example 8

Curing of polyester in accordance with Example 2b) and in combination with a vinyl ester.

10 Table 3. The mixing ratios in parts per weight for the components included in the lacquer formulations in accordance with Example 8a).

	8a)
Polyester 2b	76.5
DVAP	23.5

15

By reactivity is meant the radiation dose required to achieve surface scratch resistance in a dry film having a thickness of 45 μm . Accordingly, the reactivity for the lacquer formulation in accordance with Example 8a) was 200 mJ/cm².

20

The curing was performed using what is known as "a medium pressure mercury arc". A radiation source of this kind produces a typical mercury emission spectre. The light intensity was measured with a UVIMAP from EIT instruments. At a band speed of 10 m/min, the light intensity, measured in the area 320-400 nm, is 80-100 mW/cm².

25

4% photo initiator Darocur 1173, and 100 ppm inhibitor parabenzoquinone was added to the mixtures in accordance with Example 8a). Both were calculated on dry weight.

5 The molar ratio between the unsaturation in the vinyl ester (the co-monomer) and the ethylenical unsaturation in the polyester is 1:1.

10 The Examples which have been described in the above, shall not be considered as limiting to the invention. Hence, a number of further variants and modifications are conceivable within the scope of the appended claims.

CLAIMS

5

1. A photopolymerisable polyester composition comprising an ethylenically unsaturated polyester and a co-monomer, characterized in that the co-monomer is an alkenyl ether, an alkenyl ester, an n-alkenyl-amine or an
10 n-alkenyl-amide, or a mixture of two or more of these monomer types, that the polyester and/or the co-monomer is terminated with at least one bulky and/or hydrogen donating, monofunctional alcohol, and that the molar ratio between the degree of unsaturation of the unsaturated
15 polyester and the degree of unsaturation of the co-monomer is 0.7-1.3, preferably 0.9-1.1.

2. A composition according to claim 1, characterized in that the co-monomer exists
20 in a mixture with the unsaturated polyester.

3. A composition according to claim 1 or 2, characterized in that at least a part of the co-monomer is chemically incorporated in the unsaturated
25 polyester.

4. A composition according to any one of claims 1-3, characterized in that the functionality of the unsaturated polyester is greater than 1, preferably
30 greater than 1.3.

5. A composition according to any one of the preceding claims, characterized in that the functionality of
35 the co-monomer is between 1 and 4.

6. A composition according to any one of the preceding claims, characterized in that the bulky, hydrogen
40 donating, monofunctional alcohol is benzyl alcohol.

7. A composition according to any one of the preceding claims,
c h a r a c t e r i z e d i n that it further contains an emulsifier.

5

8. A composition according to claim 7,
c h a r a c t e r i z e d i n that the reactive emulsifier is an oligomer based on polyethylene glycol with a molecule weight between 200 and 6000 g/mol and preferably
10 between 200 and 2000 g/mol.

9. A composition according to claim 8,
c h a r a c t e r i z e d i n that the chain ends of the emulsifier have been terminated with a bulky and/or
15 hydrogen donating monofunctional alcohol.

10. A composition according to claim 7 or 8,
c h a r a c t e r i z e d i n that the emulsifier exhibits at least one ethylenical unsaturation.

20

11. A composition according to any one of the preceding claims,
c h a r a c t e r i z e d i n that the co-monomer is an alkenyl ether having a mean functionality which is greater
25 than 1 and less than 4.

12. A composition according to any one of the preceding claims,
c h a r a c t e r i z e d i n that the acid value in the binder composition is less than 10 mg KOH/g and preferably
30 less than or equal to 2 mg KOH/g.

13. A composition according to any one of the preceding claims,

c h a r a c t e r i z e d i n t h a t t h e u n s a t u r a t e d g r o u p s
i n t h e u n s a t u r a t e d p o l y e s t e r c o n s i s t o f m a l e i c a n d / o r
f u m a r i c g r o u p s .

- 5 14. A composition according to any one of the preceding
 claims,
 c h a r a c t e r i z e d i n t h a t i t e x i s t s i n t h e f o r m
 o f a w a t e r e m u l s i o n .
- 10 15. A composition according to any one of the preceding
 claims,
 c h a r a c t e r i z e d i n t h a t i t c o m p r i s e s o l i g o m e r s
 o f t h e b u l k y , t e r m i n a l , m o n o f u n c t i o n a l a l c o h o l .
- 15 16. A lacquer or paint formulation,
 c h a r a c t e r i z e d i n t h a t i t c o m p r i s e s a b i n d e r
 c o m p o s i t i o n a c c o r d i n g t o a n y o n e o f c l a i m s 1 - 1 5 .
- 20 17. A lacquer or paint formulation according to claim 16,
 c h a r a c t e r i z e d i n t h a t i t f u r t h e r c o m p r i s e s
 a p h o t o - i n i t i a t o r .

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 97/01087

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 283/01, C09D 167/06 // C08F 299/04
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F, C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4921883 A (JÜRGEN MEIXNER ET AL), 1 May 1990 (01.05.90), abstract, claims 1-2 --	1-17
A	EP 0574776 A1 (WOLFF WALSRÖDE AKTIENGESELLSCHAFT), 22 December 1993 (22.12.93), claims 1-2, 7, 10 --	1-17
A	EP 0322808 A2 (PPG INDUSTRIES, INC.), 5 July 1989 (05.07.89), abstract -- -----	1-17

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

- * Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

22 Sept 1997

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Name and mailing address of the ISA/

Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Barbro Nilsson

Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SE 97/01087

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